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# Estimating Concentrations of Road-Salt Constituents in Highway-Runoff from Measurements of Specific Conductance

By GREGORY E. GRANATO and KIRK P. SMITH

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## CONVERSION FACTORS AND WATER QUALITY UNITS

### CONVERSION FACTORS

<b>Multiply</b>	<b>By</b>	<b>To obtain</b>
centimeter (cm)	0.3937	inch
liter (L)	0.2642	gallon
kilogram (kg)	2.205	pound avoirdupois

Temperature in degrees Celsius (°C) may be converted to degrees Fahrenheit (°F) as follows:  
 $^{\circ}\text{F}=1.8^{\circ}\text{C}+32$

### WATER QUALITY UNITS

Chemical concentration is given in units of milligrams per liter (mg/L) or milliequivalents per liter (meq/L). Milliequivalents per liter are units expressing the number of electron-moles of a solute per unit volume (liter). A mole is the mass in grams numerically equal to the atomic mass of a given element. Milligrams per liter are units expressing the mass of the solute per unit volume (liter) of water. Milligrams per liter is equivalent to “parts per million.”

Specific conductance is given in microsiemens per centimeter at 25 degrees Celsius ( $\mu\text{S}/\text{cm}$  at 25°C).

# Estimating Concentrations of Road-Salt Constituents in Highway-Runoff from Measurements of Specific Conductance

By Gregory E. Granato *and* Kirk P. Smith

## Abstract

Discrete or composite samples of highway runoff may not adequately represent in-storm water-quality fluctuations because continuous records of water stage, specific conductance, pH, and temperature of the runoff indicate that these properties fluctuate substantially during a storm. Continuous records of water-quality properties can be used to maximize the information obtained about the stormwater runoff system being studied and can provide the context needed to interpret analyses of water samples.

Concentrations of the road-salt constituents calcium, sodium, and chloride in highway runoff were estimated from theoretical and empirical relations between specific conductance and the concentrations of these ions. These relations were examined using the analysis of 233 highway-runoff samples collected from August 1988 through March 1995 at four highway-drainage monitoring stations along State Route 25 in southeastern Massachusetts.

Theoretically, the specific conductance of a water sample is the sum of the individual conductances attributed to each ionic species in solution—the product of the concentrations of each ion in milliequivalents per liter (meq/L) multiplied by the equivalent ionic conductance at infinite dilution—thereby establishing the principle of superposition. Superposition provides an estimate of actual specific conductance that is within measurement error throughout the conductance range of many natural waters, with errors of less than  $\pm 5$  percent below 1,000 microsiemens per centimeter

( $\mu\text{S}/\text{cm}$ ) and  $\pm 10$  percent between 1,000 and 4,000  $\mu\text{S}/\text{cm}$  if all major ionic constituents are accounted for.

A semi-empirical method (adjusted superposition) was used to adjust for concentration effects—superposition-method prediction errors at high and low concentrations—and to relate measured specific conductance to that calculated using superposition. The adjusted superposition method, which was developed to interpret the State Route 25 highway-runoff records, accounts for contributions of constituents other than calcium, sodium, and chloride in dilute waters. The adjusted superposition method also accounts for the attenuation of each constituent's contribution to conductance as ionic strength increases. Use of the adjusted superposition method generally reduced predictive error to within measurement error throughout the range of specific conductance (from 37 to 51,500  $\mu\text{S}/\text{cm}$ ) in the highway runoff samples. The effects of pH, temperature, and organic constituents on the relation between concentrations of dissolved constituents and measured specific conductance were examined but these properties did not substantially affect interpretation of the Route 25 data set.

Predictive abilities of the adjusted superposition method were similar to results obtained by standard regression techniques, but the adjusted superposition method has several advantages. Adjusted superposition can be applied using available published data about the constituents in precipitation, highway runoff, and the deicing chemicals applied to a highway. This

semi-empirical method can be used as a predictive and diagnostic tool before a substantial number of samples are collected, but the power of the regression method is based upon a large number of water-quality analyses that may be affected by a bias in the data.

## INTRODUCTION

Specific conductance is one of the most commonly measured and most useful properties of water (Miller and others, 1988), but applications of relations between the concentrations of chemical constituents and specific conductance are not well advanced, and many interpretations are qualitative (Smedley, 1980). Improved theoretical and empirical relations between measured constituent concentrations and specific conductance would improve interpretations in many hydrologic studies.

Specific conductance is a physical property of aqueous solutions. The ability of pure water to conduct an electric current is very low (Hem, 1982). In aqueous solutions, electrical current is conducted by charged ions moving hydrodynamically through the relatively nonconductive solvent (Smedley, 1980; Hem, 1982; Miller and others, 1988). The principal factors that affect the measured specific conductance of solutions include concentrations of dissolved ions; temperature; physical and thermodynamic properties of individual ions, such as ionic radius, charge, and mobility; properties of the solvent, such as viscosity and dielectric constant; and ion-ion and ion-solvent interactions (Smedley, 1980; Hem, 1982; Miller and others, 1988; Greenberg and others 1992). These factors, the thermodynamic properties of natural waters, and interactions among water molecules and dissolved constituents vary as a function of temperature and concentration (Harned and Owen, 1958; Smedley, 1980; Miller and others, 1988; Hughes and others, 1994). Therefore, prediction of conductivity is complicated by variations in the physical and chemical properties of natural waters.

A sound method for interpretation of specific conductance in continuous records is needed to accurately determine annual salt loads in highway runoff. In highway-drainage systems, lack of base flow, uncertainty in dates and times of expected precipitation, and the short time scale of runoff and the "first-flush" phenomenon often preclude a meaningful

manual-sampling program. Also, flow data are needed for surface-water quality assessments because concentrations and resultant loads of many constituents are affected by changes in flow (Norris and others, 1990).

At monitoring sites, continuous records of measured water stage and specific conductance can provide a useful component of water-quality monitoring programs if used carefully and calibrated by periodic solute analyses. Continuous records of stage—the measured water level used to calculate the flow—and specific conductance can minimize sample collection and analysis costs and maximize the quality and quantity of information obtained about a system (Gurnell and others, 1994). Concentrations and loads of individual ionic constituents may be estimated from continuous records of specific conductance, stage, and other physical properties, because, in many hydrologic systems, ionic composition remains nearly constant although concentrations vary with dilution (Lind, 1970). Estimates can be made using these continuous records and available water analysis data and (or) knowledge of common sources for ions such as road salt or naturally occurring minerals.

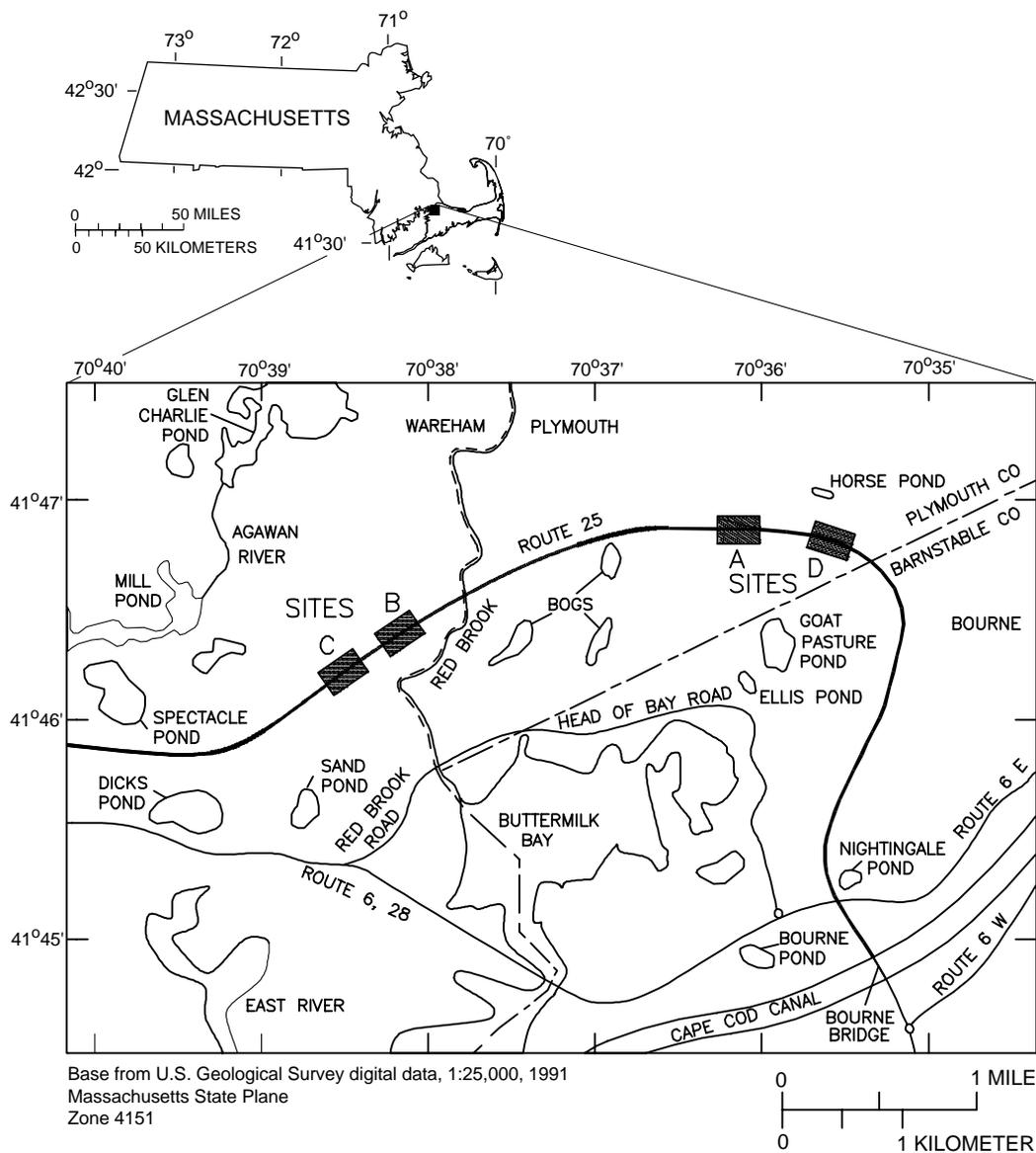
The theoretical and empirical methods developed herein may have other potential uses for estimating loads and concentrations of water-quality constituents from continuous records of stage and conductance collected with automated surface- or ground-water monitoring systems. These interpretive methods may also be used in a quality-assurance/quality-control (QA/QC) program to verify chemical analyses of discrete water samples (Miller and others, 1988). Results of a laboratory analysis may be examined by calculating a conductance based upon the measured analytes and comparing this value to the measured conductance to detect differences that are larger than expected measurement error.

The purpose of this paper is to develop and compare theoretical and empirical methods used to estimate concentrations of the road-salt constituents calcium, sodium, and chloride on the basis of continuous records of specific conductance of highway runoff. Effects of high constituent concentrations, extreme pH (less than 5 or greater than 9 standard pH units), fluctuations in temperature, or the presence of organic chemicals in solution on measured conductance are also explored to guide choices in adjustments to the quantitative relations among these properties and constituents. Use of theoretical and

empirical methods to estimate conductance from measured concentrations of major constituents is also discussed for interpretive use and analytical QA/QC.

The data used in this report were collected in a study done by the U.S. Geological Survey (USGS), in cooperation with the Massachusetts Highway Department (MHD), to investigate the relative effectiveness of four highway drainage designs in preventing contamination of ground water by road salt (Church and others, 1996). For this study, highway-runoff data were collected from 1987 through 1996.

The study was conducted along State Route 25 in a rural area of southeastern Massachusetts (fig. 1). State Route 25 is a six-lane, asphalt-surfaced highway with an annual average daily traffic volume of about 28,000 vehicles per day. The highway overlies a sand and gravel aquifer that is a source of public and agricultural water supplies. Continuous records of specific conductance and water stage measured in flumes emplaced in the highway drainage system were used to estimate the salt loads in runoff diverted by the highway-drainage systems (Church and others, 1996).



**Figure 1.** Location of study area and test sites A, B, C, and D along State Route 25 in southeastern Massachusetts.

## FIELD AND LABORATORY METHODS

During the Route 25 study, highway runoff was monitored in a calibrated Palmer-Bowlus flume built within the trunkline drainage pipe of each system. Monitoring probes, including pH, water temperature, a low-range [0–10,000 microsiemens per centimeter ( $\mu\text{S}/\text{cm}$ )] and a high-range (0–100,000  $\mu\text{S}/\text{cm}$ ) conductance probe were mounted close to each other in a small backwater pool in the approach section of the flume. Probes were emplaced about 3 cm below the elevation of the flume throat to minimize spatial variation, probe fouling, and response time to runoff. The intake orifice of the water-sampling apparatus was placed immediately downstream of the throat section to take advantage of the mixing action of the flume throat.

The monitoring system was controlled by a battery-powered datalogger. Stage and water-quality probe readings were recorded hourly when there was no flow. An increase in measured stage activated the program to record stage and water-quality probe readings at a minimum frequency of 10 minutes and a maximum frequency of 1 minute in response to the rate of change in stage and specific conductance. The automated sampler was triggered by changes in specific conductance while the stage exceeded the minimum threshold. Each sample was recorded as a sequentially numbered event with collection time and probe readings.

Laboratory analyses for dissolved concentrations of calcium, sodium, and chloride, and for specific conductance were completed for 233 discrete highway-runoff samples collected in the study area from August 1988 through March 1995. Salt samples were collected from the local MHD maintenance facility and some highway-runoff samples were collected for analysis of major and trace constituents to characterize the road-salt runoff (Granato, 1996). The samples were analyzed according to standard methods (Fishman and Friedman, 1989) at the U.S. Geological Survey National Water-Quality Laboratory in Arvada, Colorado.

The QA/QC program for this study included: (1) regular maintenance and calibration of the field probes; (2) participation in standard USGS QA/QC programs; (3) repetitive laboratory analysis of discrete samples; (4) calibration measurements using standard solutions; and (5) check measurements using

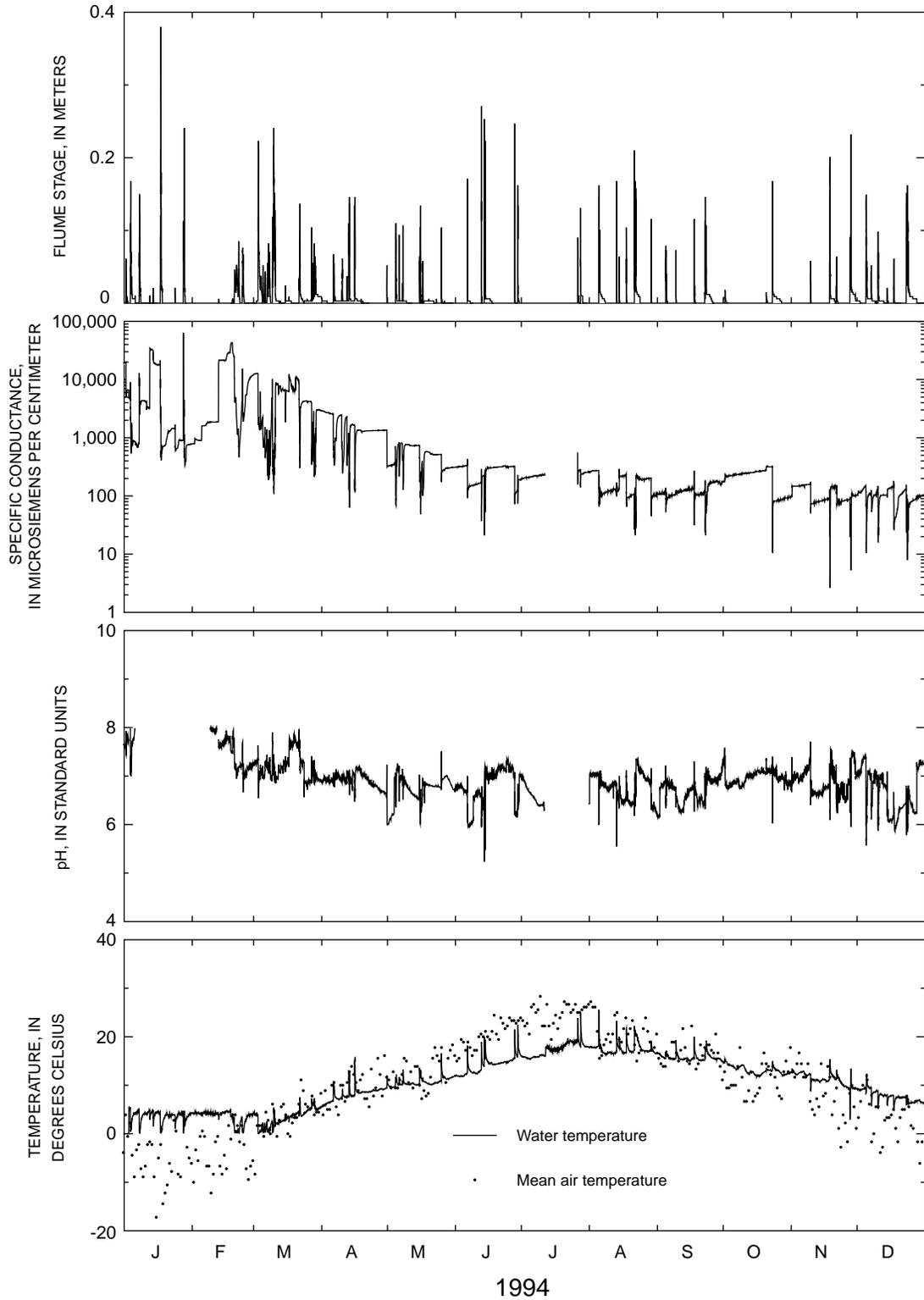
independent field and laboratory probes. Analytical methods for determining ionic concentrations were reported to be accurate to within the range of  $\pm 3$  to  $\pm 12$  percent for major ions, depending on the ionic concentration in solution and the analytical method used (Fishman and Friedman, 1989). The accuracy of measurements by the conductance probes, as determined from calibration and check measurements, was about  $\pm 5$  to 10 percent for the period of record and  $\pm 2$  to 5 percent during the period 1993–96.

## HIGHWAY-RUNOFF MONITORING RECORDS

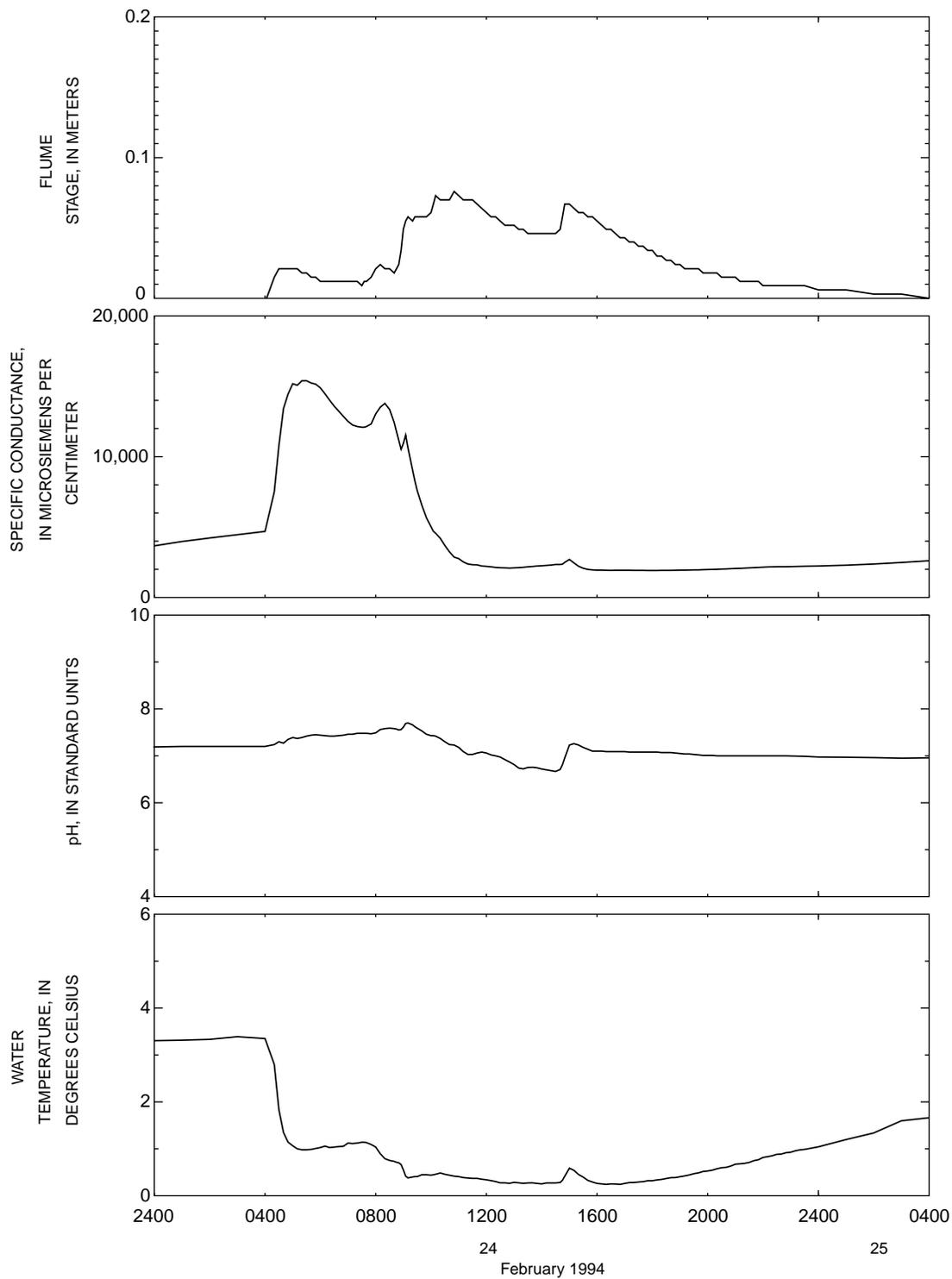
Stage, specific conductance, pH, water temperature, and air temperature were recorded continuously at four highway-runoff monitoring stations during this study. Changes in measured stage, pH, and water temperature were used separate from, or together with specific conductance to determine the type of runoff event and hydrologic response. The data collected during 1994 at monitoring station B619 (fig. 2) were considered typical of highway runoff during the study period (Church and others, 1996).

The hydraulic characteristics of the highway drainage system were indicated by the record of flume stage (fig. 2). The drainage area was a paved highway surface with runoff contributions from grass shoulders and a grass median strip. Therefore, there was no base flow. Runoff events—indicated by spikes on the graph of water stage—were caused by either precipitation or snowmelt. Runoff changed rapidly with variations in precipitation (fig. 3).

During the study period, specific conductance of highway runoff ranged from 2.69 to 63,275  $\mu\text{S}/\text{cm}$  in the continuous monitoring records and from 37 to 51,500  $\mu\text{S}/\text{cm}$  in the 233 discrete highway-runoff samples. By comparison, values of specific conductance reported in published materials were 0.5 to 3  $\mu\text{S}/\text{cm}$  for deionized water (Greenberg and others, 1992), 2 to 195  $\mu\text{S}/\text{cm}$  for regional precipitation (Gay and Melching, 1995), 50 to 1,500  $\mu\text{S}/\text{cm}$  for potable water (Greenberg and others, 1992), about 50,000  $\mu\text{S}/\text{cm}$  for seawater, and up to 225,000  $\mu\text{S}/\text{cm}$  for brines (Hem, 1992).



**Figure 2.** Highway-runoff data collected at monitoring station B619 during 1994 along State Route 25, southeastern Massachusetts.



**Figure 3.** Highway-runoff data collected at monitoring station B619 along State Route 25, southeastern Massachusetts, during a winter storm, February 1994.

The chemical characteristics of highway-runoff were indicated by the specific-conductance record (fig. 2). Application of road salt to the highway before or during storms caused large increases of specific conductance in highway runoff, as was apparent during the last storm in February, 1994 (fig. 3). Measurements of runoff quality from many storms, such as the storms that began on August 13 and 15, 1994, indicated a first flush of water that had a higher specific conductance followed by more dilute water (fig. 4), a pattern characteristic of many highway drainage systems (Barrett and others, 1993). The gradual increase in specific conductance between storm events indicated evaporative concentration of waters in the small backwater pool above the flume throat (fig. 4). In July, 1994, the flume was drained for maintenance; therefore, the probes were dry until the next storm.

Records of measured pH indicated that runoff had substantial in-storm and between-storm variations (with measured pH ranging from about 5.1 to 8.0 standard pH units) but was generally a nearly neutral solution (fig. 2). For example, a substantial drop in pH (from about 6.8 to 5.5 standard pH units) was recorded for the storm on August 13, 1994, but measured pH increased (from about 6.3 to 7.0 standard pH units) during the next storm (fig. 4). Although the pH record in the winter of 1994 for station B619 was incomplete, records from past years and other stations indicate that road salts did not cause substantial changes in pH of highway runoff in the drainage system.

Records of temperatures also were used in the interpretation of specific conductance (fig. 2). The temperatures of air and runoff-water indicated the type of event (rain, snow, or snowmelt), and were essential in applying corrections to conductance measurements; incorrect temperature compensation can be the greatest source of error in conductance measurements (Hem, 1982). Measured air and runoff temperatures indicated a beneficial temperature buffering provided by a buried highway-drainage system. During runoff, the flume-water temperature reflected the mean daily outside air temperature but not the daily extremes (fig. 2).

## THEORETICAL AND EMPIRICAL ANALYSES OF SPECIFIC CONDUCTANCE DATA

### Regression Analysis

Regression analysis, which defines the mathematical relation between two (or more) variables is the most commonly used method to relate specific conductance to concentrations of dissolved constituents. Regression results can provide reasonable estimates for individual water-quality variables in a given system (Hem, 1992). Data can be examined using standard regression techniques, free of misleading preconceptions (Helsel and Hirsch, 1992). An established regression equation may be used for all monitoring stations in an area, and may be useful for estimation at stations where complete data sets are not available (Cain, 1987).

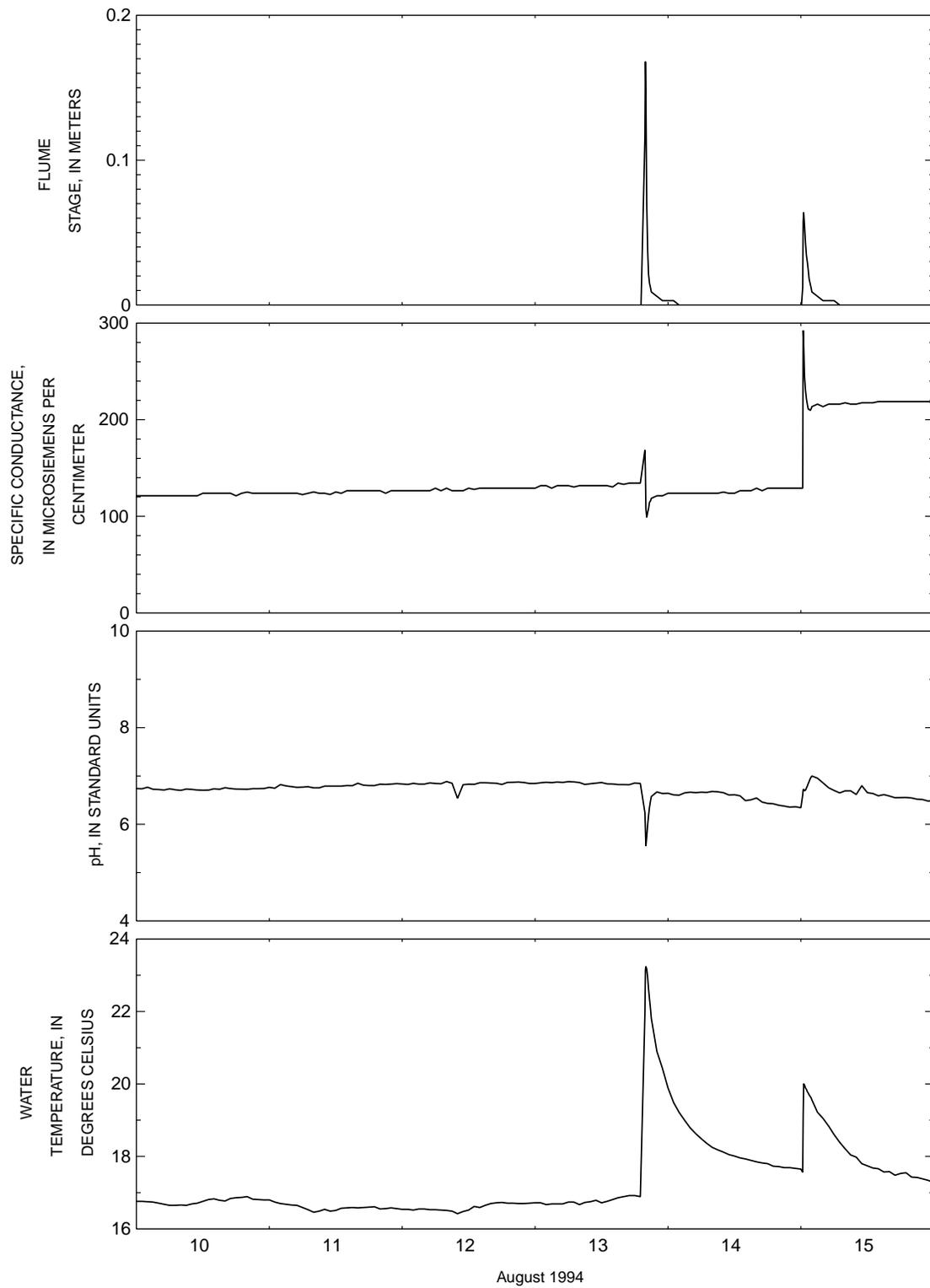
Constituents of road salt account for about 67 percent of the chemical constituents in highway runoff on an annual basis (Harned, 1988). Therefore, calcium, sodium, and chloride concentrations and specific conductance have a high degree of covariance (fig. 5). The regression model known as the line of organic correlation (Helsel and Hirsch, 1992) was chosen for use here because it minimizes errors in both the x and y directions, producing a unique equation that can be used to predict either variable from the other. The line of organic correlation follows the form:

$$(y_i - y) = \text{sign}(r) \times \frac{S_y}{S_x} \times (x_i - x), \quad (1)$$

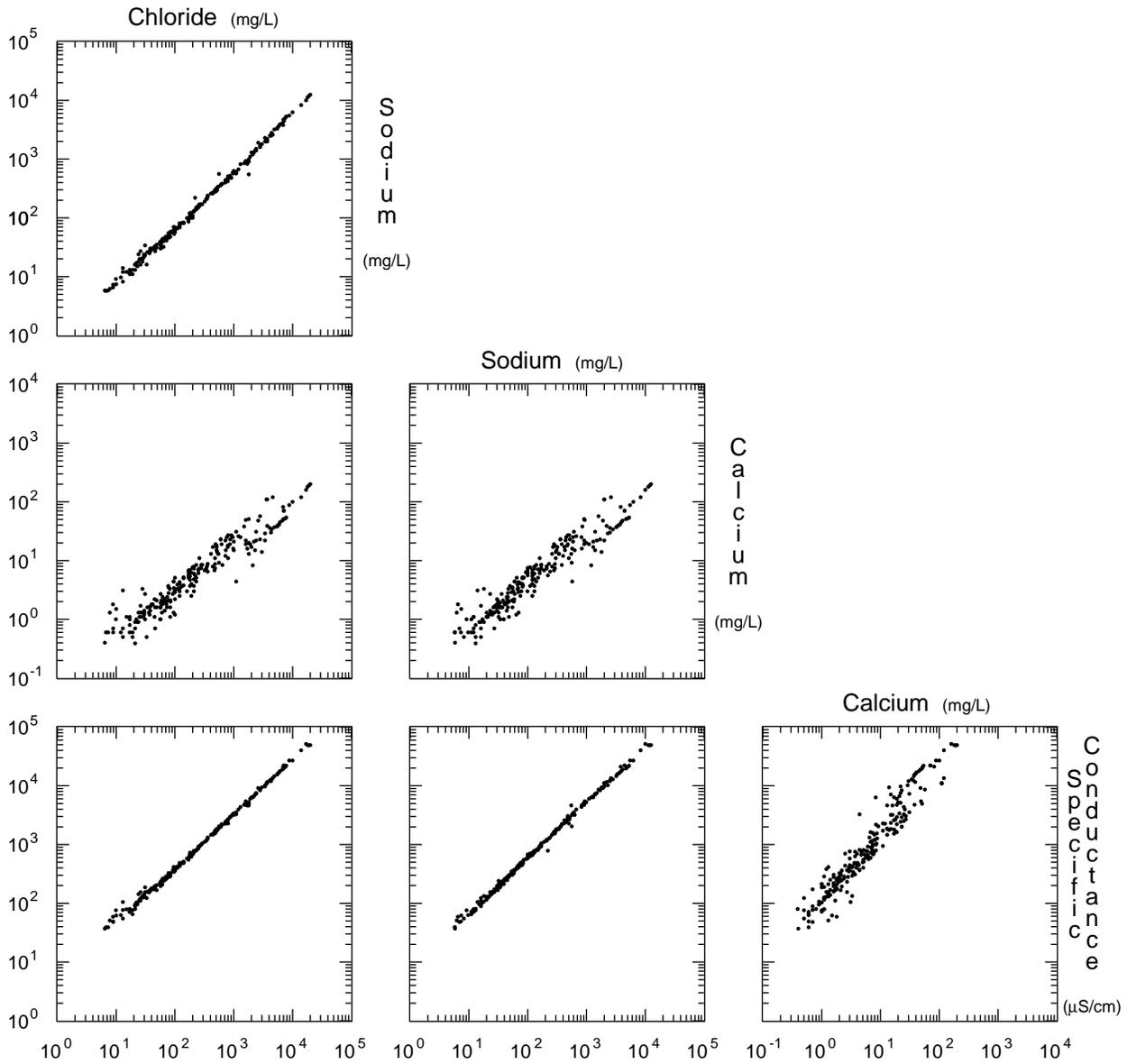
where

- $y_i$  is the predicted variable,
- $y$  is the mean of the y population,
- $\text{sign}(r)$  is the sign of the linear correlation coefficient,
- $S_y$  is the standard deviation of the y population,
- $S_x$  is the standard deviation of the x population,
- $x_i$  is the predictor variable, and
- $x$  is the mean of the x population.

High R-square values and residual plots indicate excellent predictive abilities for equation variables presented in table 1.



**Figure 4.** Highway-runoff data collected at monitoring station B619 along State Route 25, southeastern Massachusetts, during an antecedent dry period and two summer storms, August 1994.



**Figure 5.** Relations between calcium, sodium, and chloride concentrations, and specific conductance in 233 highway-runoff samples collected from August 1988 through March 1995 along State Route 25, southeastern Massachusetts.

Regression models also have disadvantages. The predictive ability of a regression model is a function of the number and distribution of available measurements from the population being studied. If used without an appreciation for relevant physical principles and a knowledge of the data set, regression may be misleading or may under-utilize the available data in the search for the best interpretation (Helsel and

Hirsch, 1992). For example, multicollinearity—where the independent variables are correlated among themselves (Helsel and Hirsch, 1992)—among the road-salt constituents calcium, sodium, and chloride would be a problem for interpretations based on a multiple-linear regression equation that predicts specific conductance from measured values of all three constituents.

**Table 1.** Regression statistics used to compute the line of organic correlation between the log transformations of specific conductance, calcium, sodium, and chloride

[--, no data]

Constituent	Mean	Standard deviation	Pearson's r	R <sup>2</sup>
Specific conductance	2.92	0.766	--	--
Calcium	.755	.630	0.962	0.926
Sodium	2.16	.807	.999	.998
Chloride	2.35	.836	.998	.997

## Superposition

The principle of superposition, Kohlrausch's law, states that the specific conductance of dilute electrolytic solutions can be calculated as the sum of the equivalent ionic conductances of all anions and cations in solution (Harned and Owen, 1958; Hem 1982). The equivalent ionic conductance at infinite dilution for each individual ion in solution was derived from observations that different combinations of ions in electrolytic solutions showed characteristic curves that approached asymptotic values with increasing dilution (Harned and Owen, 1958). Others also developed the principle of superposition using the Debye-Hückel model of electrolyte solutions by assuming that each ion is a hard sphere migrating in a dielectric continuum (Smedley, 1980).

To calculate the specific conductance of an aqueous solution by superposition, one simply sums the individual conductances attributed to all major ionic constituents in solution. The individual conductance of each ionic constituent in solution is the product of the concentration times the equivalent ionic conductance at infinite dilution for that ionic constituent. The equation is:

$$cc = \sum_{i=1}^n (c_i \times ec_i), \quad (2)$$

where

$cc$  is specific conductance calculated by superposition, in microsiemens per centimeter at 25 degrees Celsius;

$n$  is the number of major ions in solution;

$c_i$  is the concentration of the  $i$ th major ionic constituent, in milliequivalents per liter; and

$ec_i$  is the equivalent ionic conductance at infinite dilution for the  $i$ th ionic constituent, in microsiemen-liters per centimeter-milliequivalent at 25 degrees Celsius.

The equivalent ionic conductance at infinite dilution is readily obtainable from published materials for most major constituents in aqueous systems (Harned and Owen, 1958; Lind, 1970; Weast and others, 1985). Equivalent ionic conductances at infinite dilution for some major ions are presented in table 2. Although values for some trace elements are not readily available from published materials, the minor contribution of trace ions may be ignored (Lind, 1970).

Examination of calculated specific-conductance values from analyses of water samples indicates that estimates of measured specific conductance below 1,000  $\mu\text{S}/\text{cm}$  by superposition are accurate when a complete major ion analysis is available (table 2). In this conductance range, the difference between calculated and measured specific conductance is within the error of  $\pm 5$  percent expected for conductance probes (Hem, 1982) and is often close to the error in charge balance of the laboratory analysis. The difference between measured and calculated specific conductance increases with increasing concentrations of dissolved constituents, but does not exceed 10 percent until specific conductance approaches 4,000  $\mu\text{S}/\text{cm}$ . Therefore, superposition provides a good approximation throughout the specific-conductance range of most natural waters. The difference increases, however, from about 3 percent at a specific conductance of 757  $\mu\text{S}/\text{cm}$  to about 12 percent at 4,730  $\mu\text{S}/\text{cm}$ , and to about 26 percent at 10,190  $\mu\text{S}/\text{cm}$ , indicating that measured specific conductance does not increase linearly with increasing solute concentrations (table 2).

## Concentration Effects

Superposition was applied to analyses of calcium, sodium, and chloride for 233 highway-runoff samples collected from August 1988 through March 1995 (fig. 6). Plots of calculated specific conductance and the percent error of calculated values over the range of measured specific conductance indicated systematic error that varied with concentration. Below 500  $\mu\text{S}/\text{cm}$  an apparent "low-concentration effect"—underestimation of specific conductance—was caused by the omission of major ions other than calcium, sodium, and chloride. Above 2,000  $\mu\text{S}/\text{cm}$ , calculated values increasingly overestimated measured specific conductance, an apparent "high-concentration effect." These differences, however, could be explained theoretically.

**Table 2.** Equivalent ionic conductance at infinite dilution and specific conductance calculated by superposition from the concentrations of measured constituents in samples of precipitation and highway runoff, State Route 25, southeastern Massachusetts, during several storms from 1991 through 1995

[Equivalent ionic conductance at infinite dilution from Weast and others (1985). Two highway runoff samples were collected at different times during a storm on February 28, 1995.  $\mu\text{S}/\text{cm}$ , microsiemens per centimeter at 25 degrees celsius;  $[(\mu\text{S L})/(\text{cm meq})]$ , microsiemen-liter per centimeter-milliequivalent at 25 degrees celsius; --, no data]

Constituent	Equivalent ionic conductance at infinite dilution $[(\mu\text{S L})/(\text{cm meq})]$	Specific conductance calculated by superposition ( $\mu\text{S}/\text{cm}$ )				
		Precipitation		Highway runoff		
		3/07/91	1/07/95	3/24/93	2/28/95	2/28/95
Calcium .....	59.47	0.77	8.03	11.0	148	356
Magnesium .....	53.00	1.38	3.18	4.24	19.2	31.0
Sodium .....	50.08	14.4	78.8	283	1,850	4,570
Potassium .....	73.48	.22	1.18	.955	10.2	15.7
Bicarbonate .....	44.50	1.3	--	7.12	--	--
Hydrogen <sup>1</sup> .....	349.65	.011	.055	.174	.11	.174
Sulfate .....	80.00	2.9	11.2	15.8	55	58.3
Chloride .....	76.31	23.7	123	452	3,230	7,750
Fluoride .....	55.40	--	--	.332	--	--
Iron, ferrous .....	54.00	--	.27	.108	.216	.108
Manganese .....	53.5	.054	--	.054	--	--
Total specific conductance						
Calculated <sup>2</sup> .....		44.8	225	775	5,310	12,800
Measured .....		44	229	757	4,730	10,190
Percent difference						
Specific conductance .....		1.8	-1.71	2.41	12.4	25.6
Charge balance .....		-6.8	.93	-2.89	-3.64	-2.07

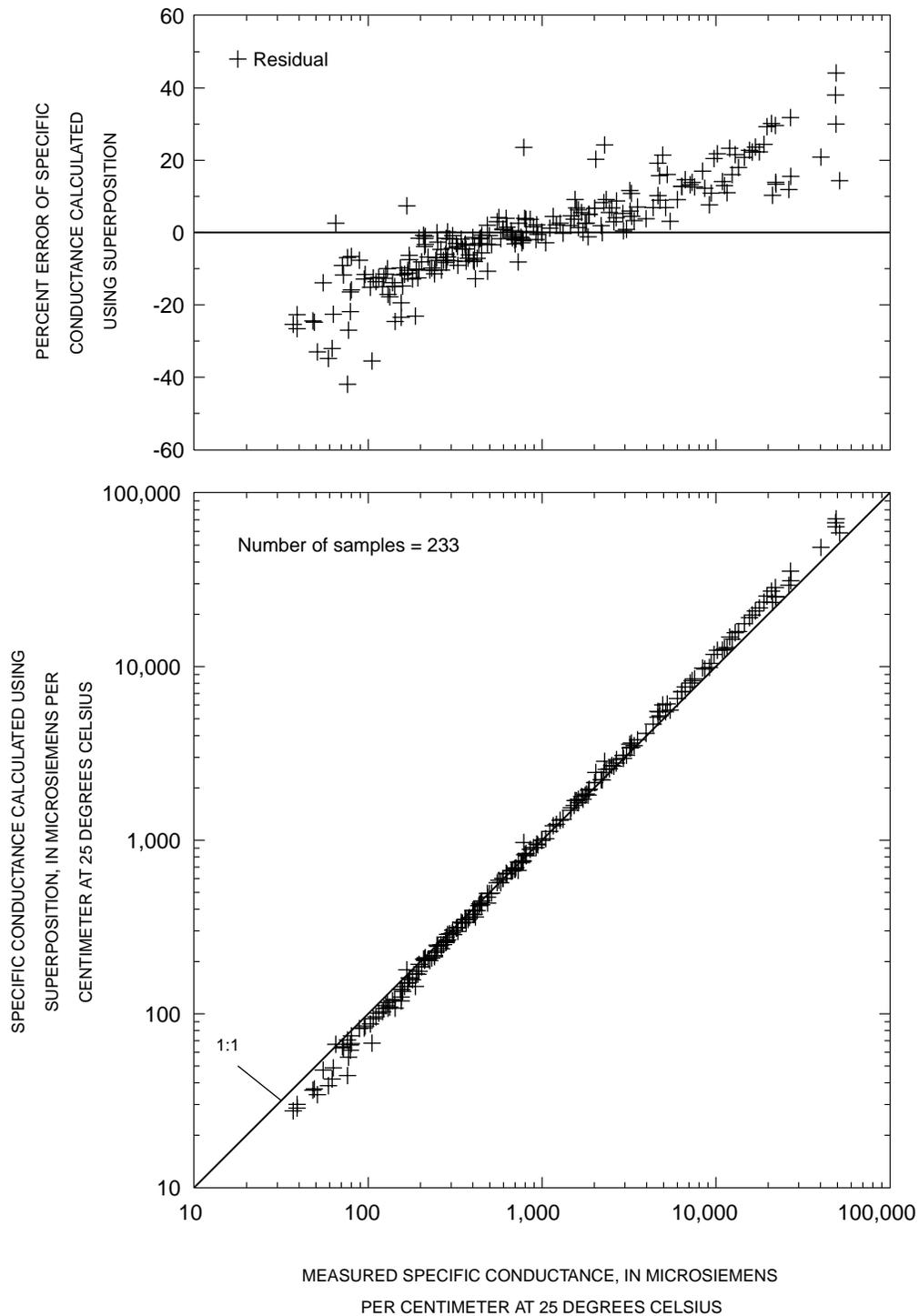
<sup>1</sup>Concentrations used for calculations were derived from pH.

<sup>2</sup>Specific conductance is calculated using equation 2.

Omission of many major constituents in most chemical analyses of water samples collected along Route 25 accounts for the apparent “low-concentration effect” in specific conductance estimates below 500  $\mu\text{S}/\text{cm}$  (fig. 6). Most chemical analyses included only calcium, sodium, and chloride as analytes in water samples collected for the Route 25 study. These analyses omitted other major constituents contributed by road salt, such as sulfate (Granato, 1996), and the other major constituents contributed by precipitation and the road surface. When measured specific conductance was less than 500  $\mu\text{S}/\text{cm}$ , the relative contribution of the other major ions to specific conductance was substantial. Therefore, the estimate of total conductance made using the superposition method with available highway-runoff analyses of calcium, sodium, and chloride was too low, hence, the “low-concentration effect.”

The error was relatively low ( $\pm 5$  percent) in the range of specific conductance from 500  $\mu\text{S}/\text{cm}$  to 2,000  $\mu\text{S}/\text{cm}$  (fig. 6). In this conductance range, the constituents measured (calcium, sodium and chloride) dominate the measured conductance, and attenuating effects caused by high concentrations are not yet pronounced.

The “high-concentration effect”—the increasing tendency of the superposition method to over estimate measured conductance above 2,000  $\mu\text{S}/\text{cm}$ —is caused by physical and chemical changes in solution properties with increasing concentrations of solutes in this range. As concentrations increase, more ions are complexed, and ionic interference becomes substantial (Harned and Owen, 1958). Attenuation of ionic mobility occurs because ion activities decrease with increases in concentrations (Hamer and DeWane, 1970; Smedley, 1980). High concentrations also affect bulk properties of the solvent, such as the viscosity and the dielectric constant, which also attenuate ionic mobility (Harned and Owen, 1958; Smedley, 1980). All these effects combine to reduce the capability of the ions in solution to transport electricity. Therefore, the measured conductance will be lower than the calculated conductance estimated by superposition (fig. 6). The “high-concentration effect” is important because substantial amounts of road salt are transported in highway runoff when the specific conductance is above 2,000  $\mu\text{S}/\text{cm}$ .



**Figure 6.** Measured specific conductance, specific conductance calculated by superposition, and percent error of calculated values for 233 highway-runoff samples collected along State Route 25, southeastern Massachusetts, from August 1988 through March 1995.

## Other Effects

Concentration effects may not be the only cause for error in estimating specific conductances on the basis of water-quality data. Other factors include the effects of variations in pH and temperature, and the effect of organic chemicals on the measured conductance. These effects were examined for their application to the analysis of data from highway-runoff samples.

The effect of extreme pH on measured specific conductance can be important because the hydrogen ion is five to seven times more conductive than cations of comparable charge and size and because the hydroxide ion is two to three times more conductive than comparable anions (Johnsson and Lord, 1987). Mobility of these ions is hypothesized to be higher than ions of similar size and charge because proton transfer (similar to electron transfer in metals) augments hydrodynamic migration (Smedley, 1980). At very high salt concentrations (above 1 mol/kg), however, the reduced mole fraction of water inhibits this proton transfer (Smedley, 1980).

The theoretical contribution of the hydrogen and hydroxyl ions is shown in figure 7 with a population of about 15,000 pH measurements recorded at two highway-runoff monitoring stations along State Route 25 during 1994. The median pH measured in these two drainage systems was slightly below a neutral value of 7 standard pH units, and the range of pH for most of the population of measurements as indicated by the box and whisker plots in figure 7, was 6 to 8 standard pH units. The magnitude of the theoretical contribution of the hydrogen and hydroxyl ions to specific conductance in this pH range was less than 0.5  $\mu\text{S}/\text{cm}$  (fig. 7). The pH effect was not substantial for highway runoff monitored along State Route 25, despite the fact that regional precipitation was acidic, with a median pH of 4.4 (Gay and Melching, 1995).

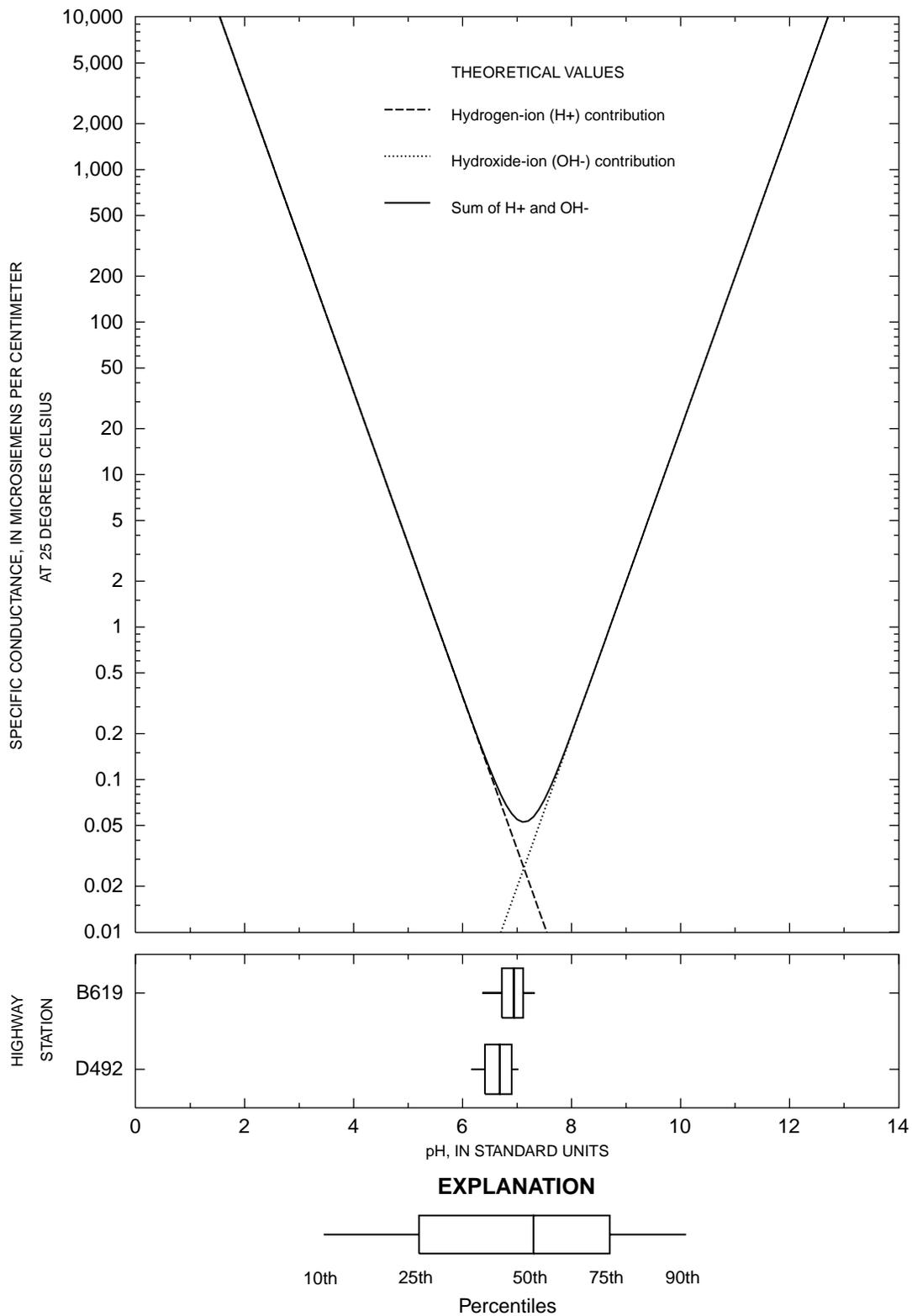
Temperature compensation can be the greatest source of error in the measurement and interpretation of specific-conductance data (Hem, 1982). Specific conductance increases by about 0.5 to 3 percent per degree above zero degrees Celsius because a comparable decrease in the viscosity and solvation of water increases the hydrodynamic mobility of ions in this temperature range (Smedley, 1980; Johnsson and

Lord, 1987; Miller and others, 1988; Fishman and Friedman, 1989; Talbot and others, 1990). The temperature effect on measured conductivity depends on ion-solvent interactions that vary with concentrations and characteristics of different ions in solution, and with the temperature (Smedley, 1980). These complications make temperature compensation very difficult.

Different methods are available to perform the necessary temperature compensation. Probes are commonly temperature-compensated using the documented temperature response of standard potassium chloride solutions. These standard temperature-compensation methods, however, may bias measured specific conductance in solutions of mixed electrolytes (Hem, 1982). The most effective way to minimize temperature compensation errors is to determine a temperature relation for water samples collected in the study area and to apply the results to records of uncompensated conductance that are later calibrated to specific conductance at 25 degrees Celsius. Temperature compensation was not a large source of error in continuous records collected along State Route 25 because the instruments were calibrated routinely at different temperatures, and temperature buffering by the buried highway-drainage system minimized the effect of temperature fluctuations.

Organic constituents in solution also can have a substantial effect on measured specific conductance. Organic constituents can attenuate the measured specific conductance of a solution by inhibiting the dissociation of electrolytes in water (Harned and Owen, 1958). Organics that do not dissociate conduct current poorly (Greenberg and others, 1992), and those that do dissociate can reduce conductivity by complexing with inorganic constituents (Drever, 1988; Smedley, 1980).

The potential magnitude of the "organic constituent effect" was measured by laboratory tests. Equivalent volumes of deionized water (used as a control to measure the effect of dilution) and reagent grade methanol and acetone were added to different samples of 100-, 1,000-, and 10,000- $\mu\text{S}/\text{cm}$  potassium chloride specific-conductance standards. After each volume was added, the specific conductance of each mixture was measured. The results show that small



**Figure 7.** Theoretical contribution of the hydrogen and hydroxyl ions and populations ( $n=15,000$ ) of pH measurements recorded at two highway-runoff monitoring stations (B619 and D492), State Route 25, southeastern Massachusetts, during 1994.

percentages of these organic constituents in solution may substantially decrease measured conductance values (fig. 8). However, the magnitude of attenuation caused by each different organic constituent depends on its particular properties (Harned and Owen, 1958; Smedley, 1980).

The attenuating effect of dissolved organic constituents on measured specific conductance was of concern because mean concentrations of total organic carbon in highway runoff vary from 2.4 to 7.7 percent of solution by mass (Barrett and others, 1993). Relations between chloride and specific conductance for 233 highway-runoff samples collected along State Route 25 were compared to relations for 33 samples of road-salt solutions created in the laboratory. The nonparametric rank sum test was applied to results of analysis from the 233 field samples and 33 laboratory samples in the specific conductance range from 20 to 50,000  $\mu\text{S}/\text{cm}$ . No significant differences were found between the sampled populations at a 95 percent confidence interval, indicating no substantial organic attenuation for this study site. Particulates bind greater than 90 percent of the total organics in highway runoff (Barrett and others, 1993), which could have reduced organic attenuation of specific conductance at this site.

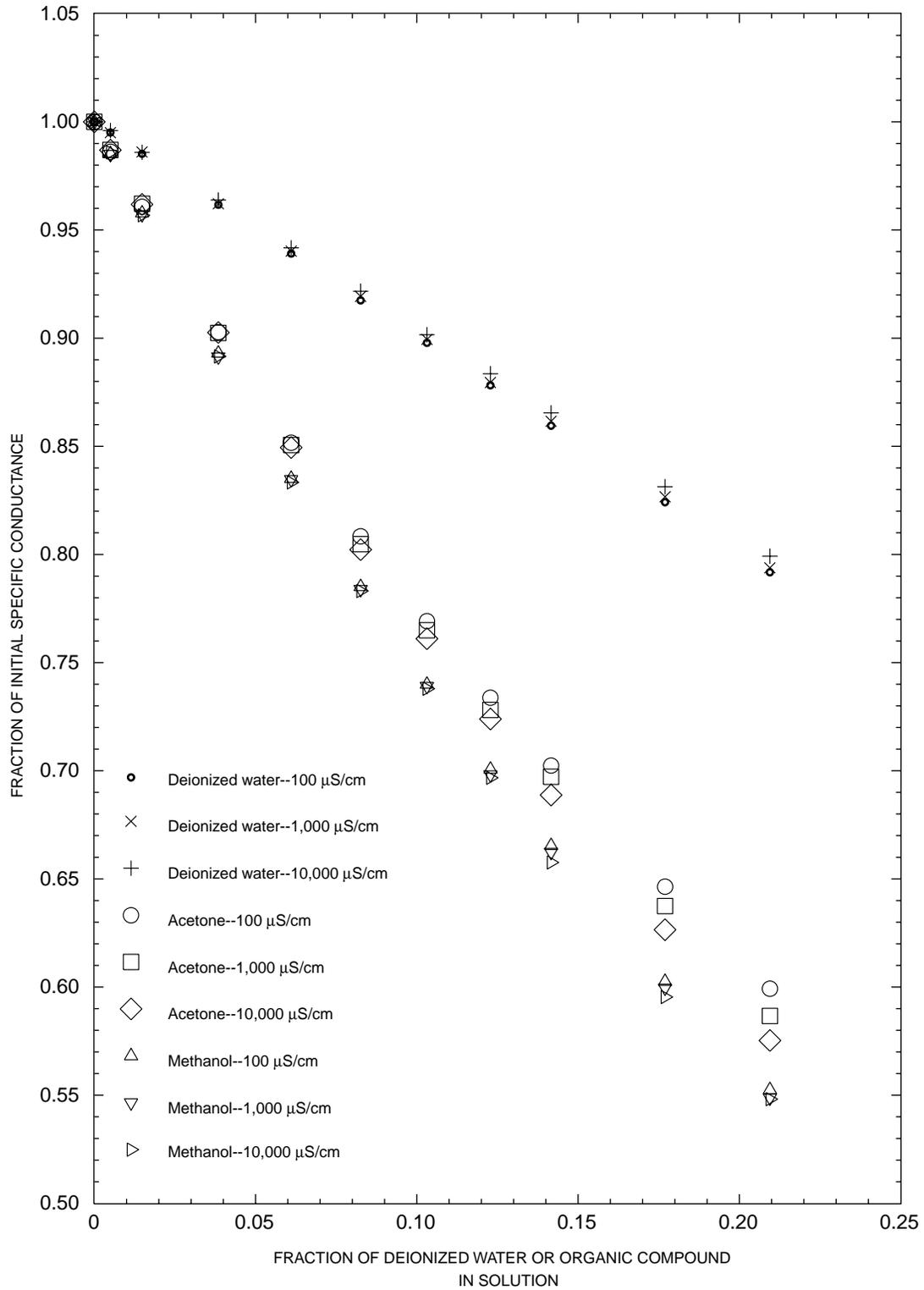
## Adjusted Superposition

Adjusted superposition, a semiempirical method, can improve quantitative relations among estimated and measured specific conductance and constituent concentrations. Although the effects of pH, temperature, and organic constituents in highway runoff at the study site did not warrant adjustment, the concentration effects shown in figure 6 were problematic. A semiempirical method was used because the physical phenomena attenuating measured conductance could not be adequately quantified using purely theoretical approaches (Harned and Owen, 1958; Smedley, 1980).

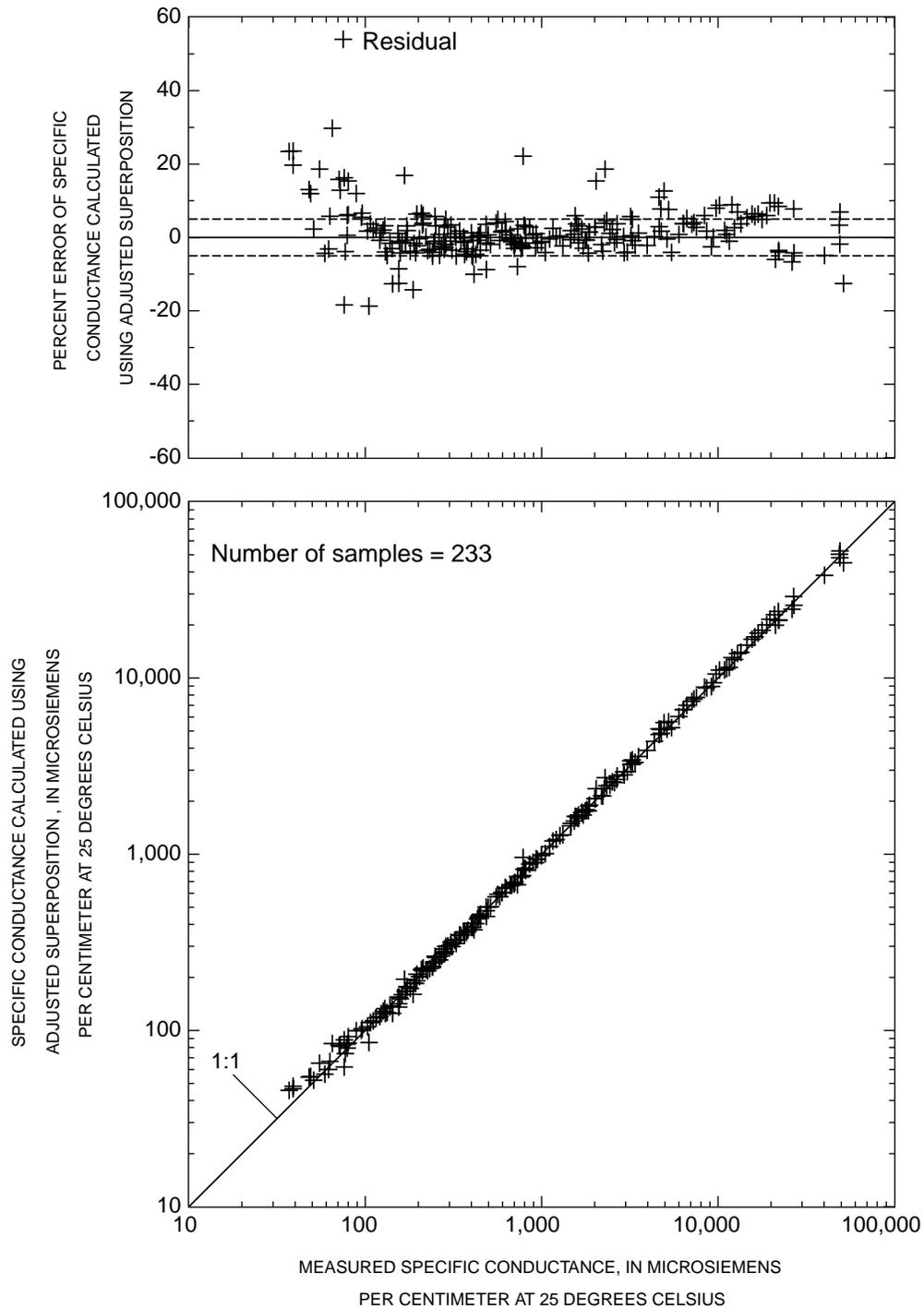
Adjustment for the “low-concentration effect”—omission of analysis for major constituents other than calcium, sodium, and chloride—on calculated specific conductance below 500  $\mu\text{S}/\text{cm}$  (fig. 6) was accomplished by estimating the contribution of the

other major constituents in precipitation to specific conductance. The total specific conductance of precipitation samples collected along State Route 25 ranged from 15 to 80  $\mu\text{S}/\text{cm}$ , of which 6 to 21  $\mu\text{S}/\text{cm}$ , respectively, was estimated to derive from the other major constituents. The contribution of the other major constituents in precipitation collected near the study area (Gay and Melching, 1995) was estimated to be from about 1.76 to about 68  $\mu\text{S}/\text{cm}$  when total measured specific conductance ranged from 2 to 195  $\mu\text{S}/\text{cm}$ , respectively. A value of 18.2  $\mu\text{S}/\text{cm}$  was estimated from median values presented by Gay and Melching (1995) as the contribution of major ions other than calcium, sodium, and chloride to measured specific conductance in precipitation. This median was chosen because precipitation-quality was similar in both studies and the data of Gay and Melching (1995) had many more analyses than the limited number available from the State Route 25 project data set. Adding this median non-salt contribution to the conductance estimated using superposition improved the predictive capability of the equation between 100 and 500  $\mu\text{S}/\text{cm}$  (fig. 9).

Empirical relations were used to account for the high-concentration effects—attenuation of the contribution to conductance by each constituent as ionic strength increases—because quantitative information (including details about inter-ionic effects and water/solute interactions for the solution in question) is usually not available. Therefore, a regression analysis was used to relate measured and estimated specific conductance values to the residual difference between measured and estimated values. This regression analysis provided the necessary information to formulate the equations for adjusted superposition. Regression equations were developed using the ordinary least squares method. It was appropriate to fix the intercept at zero because the data covered several orders of magnitude and the attenuation of each constituent's conductance at infinite dilution approaches zero with decreasing ionic strength. The independent variable was transformed to the three-halves power to linearize the residuals and improve homoscedasticity (Helsel and Hirsch, 1992).



**Figure 8.** Attenuation of measured specific conductance by soluble organic compounds.



**Figure 9.** Measured specific conductance, specific conductance calculated by adjusted superposition, and percent error of calculated values for 233 highway-runoff samples collected along State Route 25, southeastern Massachusetts, from August 1988 through March 1995.

The adjusted superposition equation developed by combining the empirical regression and the contributions from precipitation are:

$$ce = cc - 0.00097 \times cc^{3/2} + co, \quad (3)$$

where

*ce* is the specific conductance calculated by adjusted superposition, in microsiemens per centimeter at 25 degrees Celsius;

*cc* is specific conductance calculated by superposition (equation 2), in microsiemens per centimeter at 25 degrees Celsius;

*co* is the specific conductance from constituents not analyzed; in this case, 18.2 microsiemens per centimeter at 25 degrees Celsius.

Also, when the results of analysis are suspect, it would be desirable to check the analysis and(or) the measured specific conductance as a QA/QC measure. The equation:

$$cc = cm + 0.00137 \times cm^{3/2} - co, \quad (4)$$

where

*cm* is the measured specific conductance, in microsiemens per centimeter at 25 degrees Celsius,

may be used to relate the measured conductance to the theoretical specific conductance calculated by superposition.

Specific conductance may be estimated accurately from analysis of the major constituents of road salt (calcium, sodium, and chloride), if corrections are made for the major constituents omitted in the water analysis and for attenuating effects caused by increasing concentration. Estimates of specific conductance by adjusted superposition match closely the corresponding measured conductances (fig. 9). The adjustments improve the relation shown in figure 6, eliminating systematic error and generally reducing random

error to within  $\pm 5$  percent (the accuracy expected of field specific-conductance measurements). The error still evident in the estimated specific-conductance values below 100  $\mu\text{S}/\text{cm}$  can be attributed to variations in precipitation chemistry whose effect on specific conductance increases as the effect of road-salt constituent concentrations decreases.

## ESTIMATION OF ROAD-SALT CONSTITUENT CONCENTRATIONS

Specific-conductance records were used to calculate concentrations of calcium, sodium, and chloride to determine road-salt loads in highway runoff. First, adjusted superposition (equation 4) was used to convert the measured specific conductance value (*cm*) to an equivalent calculated conductance value (*cc*). Then, concentrations of each ion were estimated from the calculated conductance value (*cc*). The equation to determine constituent concentrations from the calculated conductance value includes three unknowns (concentrations of calcium, sodium, and chloride).

The equations used to estimate constituent concentrations from the calculated conductance can be solved with information about the chemical composition of the source water (in this case it was road salt in highway runoff). The equations used to derive each constituent from the calculated conductance (eq. 4) are as follows:

$$Ca = Rca \times Cl, \quad (5)$$

$$Na = Rna \times Cl, \quad (6)$$

and

$$Cl = (cc) \div [(Rna \times Cna) + (Rca \times Cca) + (1 \times Ccl)], \quad (7)$$

where

*cc* is specific conductance calculated by superposition, in microsiemens per centimeter at 25 degrees Celsius;

*Ca* is the molar concentration of calcium;

*Na* is the molar concentration of sodium;

*Cl* is the molar concentration of chloride;

*Rca* is the molar ratio of calcium to chloride, which varies with measured specific conductance;

*Rna* is the molar ratio of sodium to chloride,

(about 0.958);

*Cca* is the equivalent conductance at infinite dilution of calcium;

*Cna* is the equivalent conductance at infinite dilution of sodium; and

*Ccl* is the equivalent conductance at infinite dilution of chloride (equivalent conductances at infinite dilution are reported in table 2).

The ratios of sodium to chloride and calcium to chloride in the highway-runoff samples were used to determine the concentration of each constituent in solution because the data were available. In the absence of an extensive data set, median ratios of calcium and sodium to chloride in samples of road salt (Granato, 1996) could be used to estimate concentrations of calcium, sodium, and chloride in highway runoff from measured specific-conductance records.

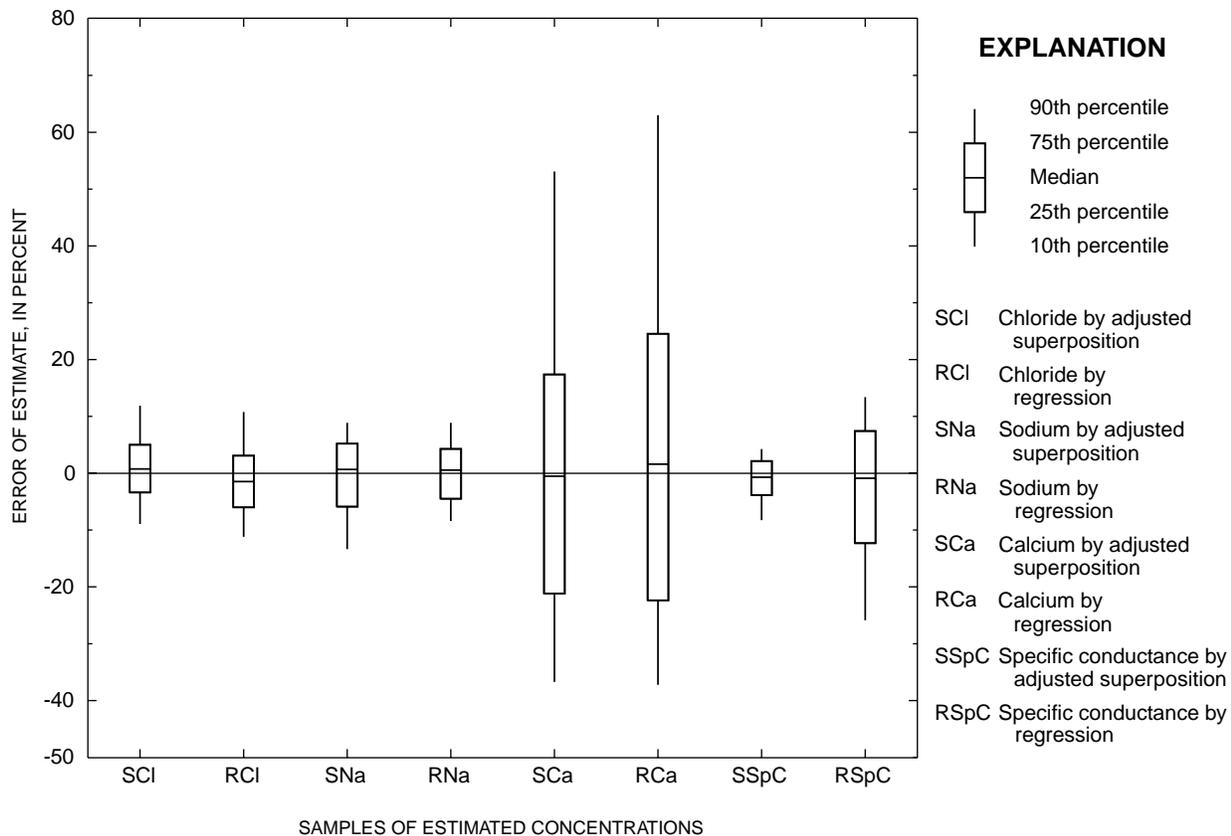
The ratio of sodium to chloride in the highway-runoff samples was relatively constant over the entire range of specific conductance (fig. 5). The median molar ratios for sodium to chloride in seawater (Hem, 1992), regional precipitation (Gay and Melching, 1995), road-salt samples (Granato, 1996), and the highway-runoff samples from the study area were 0.852, 0.906, 0.958, and, 0.963, respectively. The ratio of sodium to chloride was relatively constant even in low-conductance highway runoff because precipitation at the study site was affected by the sodium chloride from seawater. Therefore, the median ratio of sodium to chloride either in the road-salt samples or in the highway-runoff samples could be used to estimate the relation between sodium and chloride in highway runoff.

Calcium had greater variance and lower concentrations than was measured for sodium and chloride in highway runoff samples (fig. 5). In the study area, calcium chloride generally was applied to the highway surface in a premix of 80 percent sodium chloride and 20 percent calcium chloride by mass (Church, and others, 1996). During winter storms, sodium chloride, premix, or both may have been applied to the highway. The molar ratio of calcium to chloride was 0.0075 in sodium chloride and 0.097 in the premix used during the study (Granato, 1996). Calcium represented only about 2 percent by mass of

the deicing-chemicals spread each year because of the infrequent use of the calcium chloride premix. The median molar ratio of calcium to chloride in the 233 highway-runoff samples was 0.022, and about 1.5 percent of the deicing chemicals measured. The molar ratio of calcium to chloride varied substantially in coastal precipitation (between 0.009 and 0.06 from Gay and Melching, 1995) but was generally higher than in seawater (0.019 from Hem, 1992). Also, the concrete drainage system may have been a source of calcium in dilute waters. In highway-runoff samples, the molar ratio of calcium to chloride in the ranges zero to 200  $\mu\text{S}/\text{cm}$ , 200 to 1,000  $\mu\text{S}/\text{cm}$ , 1,000 to 6,000  $\mu\text{S}/\text{cm}$ , and greater than 6,000  $\mu\text{S}/\text{cm}$  were 0.038, 0.025, 0.020, and 0.0075, respectively. These ratios showed a transition from the median precipitation ratio of about 0.048 at low specific-conductance values to the ratio found in sodium-chloride road salt in the highest conductance range.

The relative precision and accuracy of calculations using adjusted superposition (eqs. 4, 5, 6 and 7) were compared to the regression equations (eq. 1) graphically (fig. 10) and statistically using the nonparametric Wilcoxon rank sum test. The estimates of chloride concentrations by adjusted superposition were significantly different and are slightly better than estimates from regression at a 95-percent confidence interval. The differences in predictive capabilities of adjusted superposition and regression for specific conductance and the constituents sodium and calcium were not significantly different at a 95-percent confidence interval.

Although the predictive abilities for regression and adjusted superposition for this data set were generally equivalent, the predictive ability of a regression relation is a function of the number and distribution of available measurements from the specific-conductance population studied. Adjusted superposition, however, can provide reasonable estimates of expected specific-conductance values and constituent concentrations from available information describing the composition of road salt, precipitation, and natural waters reported in published materials.



**Figure 10.** Comparison of the predictive ability of adjusted superposition and regression equations shown as percent error populations using 233 highway-runoff samples collected along State Route 25, southeastern Massachusetts.

## CONCLUSIONS

Highway-runoff monitoring records indicate that in highway-drainage systems, the lack of base flow, uncertainty in dates and times of expected precipitation, the short time scale of runoff, and the first flush-phenomenon may preclude a meaningful manual sampling program. Runoff records show substantial fluctuations in measured stage, specific conductance, pH, and temperature throughout the course of each storm. Continuous records of these water-quality properties provide the context needed to interpret analyses of discrete samples. Therefore, results of manual- or automatic-sampling programs may be questionable without a supporting record of real-time measurements.

Concentrations of calcium, sodium, and chloride—dissolved constituents of road salt—can be estimated in real time for the interpretation of highway-runoff monitoring records using theoretical and empirical relations between specific conductance and

constituent concentrations. If used carefully and calibrated by periodic solute analyses, continuous records of stage and specific conductance can be used to maximize the information obtained about the hydrologic system being studied while minimizing the costs of sample collection and analysis.

If information is known about the major constituents in the source water, and about the source of contaminants—either from published materials or from a sampling program—superposition can be used to provide an accurate estimate for relations between constituent concentrations and specific conductance. Briefly, the principle of superposition states that the electrical conductance measured in a water sample is a function of the sum of the conductances of all ionic constituents in solution. Relations between measured specific conductance and estimated constituent concentrations can be formulated using periodic water-quality analyses, or by using information about the composition of road-salt used in the study area when sufficient water-quality analyses are not available.

Superposition can provide an estimate that is within measurement error throughout the specific-conductance range of many natural waters (with errors of less than  $\pm 5$  percent below 1,000  $\mu\text{S}/\text{cm}$  and  $\pm 10$  percent below 4,000  $\mu\text{S}/\text{cm}$ ) if all major ionic constituents are measured.

Adjusted superposition can be used when the sources of constituents are not fully characterized, or when solutions of high conductance (greater than 4,000  $\mu\text{S}/\text{cm}$ ) are studied. For example, the median contribution of constituents other than calcium, sodium, and chloride from published values for regional precipitation (about 18.2  $\mu\text{S}/\text{cm}$ ) was used to estimate conductance in highway runoff, and this correction reduced error substantially when conductance values were below 500  $\mu\text{S}/\text{cm}$ . Adjusted superposition can also be used to reduce error when measured specific conductances are large. In this study, adjusted superposition generally reduced the error of estimates from specific conductance to  $\pm 10$  percent or less for runoff with high ionic strengths. Other factors, including temperature, pH, and the presence of organic constituents in solution, may have a substantial effect on the relation between concentrations of dissolved constituents and measured specific conductance. These other factors did not seem to affect relations between concentrations of dissolved ions and specific conductance of highway runoff in this study.

Although the predictive abilities for regression analysis and adjusted superposition are generally equivalent, regression analysis requires an extensive data set that may be expensive and time-consuming to obtain. In addition, analytical errors may define the regression model, and omissions of important constituents cannot be detected by regression. The predictive ability of regression requires many water-quality analyses over the expected range of specific conductance, whereas superposition can provide a close approximation of relations between conductance and water-quality characteristics using the molar ratios of constituents and other information available in published materials. Measurements and estimates of specific conductance can be compared to check water-quality analyses as samples are obtained and analyzed. Superposition is not affected by analytical errors that may define a regression model. Values for estimated specific-conductance that are substantially lower than

measured values may indicate that an important constituent (or constituents) has been omitted in the water-quality analysis.

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